COMBINED MICROWAVE–OPTICAL BARRIER DETERMINATION FOR MOLECULES WITH A HEAVY SYMMETRIC INTERNAL TOP: CF_3NO AND CF_3CHO

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The torsional data for CF_3NO have been reinvestigated. A model with a single degree of freedom and three adjustable parameters is sufficient to fit data to $v = 8$ in the electronic ground state. For CF_3NO we obtain $F_0 = 1.9822(42)$ cm^{-1}, $V_3 = 238.4(1.6)$ cm^{-1} and $V_6 = -5.8(1.6)$ cm^{-1} or $F_0 = 1.9894(66)$ cm^{-1}, $F_3 = -0.194(55)$ cm^{-1} and $V_3 = 239.3(1.9)$ cm^{-1}. A similar treatment for CF_3CHO gives $F_0 = 1.97(14)$ cm^{-1}, $V_3 = 305(25)$ cm^{-1} and $V_6 = -8.7(1.2)$ cm^{-1}. A need for a re-examination of the torsional fundamental is indicated for CF_3CHO. These studies support the general conclusion that for a heavy internal top the internal rotation constant, F_0, required to fit a range of torsional splittings is different from that calculated from structural considerations alone. The difference indicates a large change in F with torsional averaging.

1. Introduction

Barriers to internal rotation are conventionally obtained from spectroscopic data using an effective single-degree-of-freedom model, the reduced moment of inertia being taken from the structural parameters and the data consisting of one or more energy-level spacings. This approach works well for CH_3 tops and other light internal rotors, but gives problems when the internal rotor is of substantial mass in comparison to the molecular framework. It then becomes impossible to reconcile the pure torsional (A–E) splitting, Δ_0, obtained from microwave spectroscopy, with data obtained from far-infrared or other optical measurements. The problem moreover is not solved by simply including further terms (V_6, etc.) in the hindering potential. This situation has recently been highlighted by an extensive assignment of torsional progressions in the laser-induced fluorescence spectrum of CF_3NO [1]. A discrepancy has also been apparent for some time in the case of CF_3CHO [2]. These studies indicate that some revision of the model is required. It transpires that the single-degree-of-freedom model is appropriate to the heavy top internal-rotor case provided that the internal-rotation constant used to fit the spectrum is allowed to differ from that computed conventionally from the structure.

2. Hamiltonian

The CF_3NO and CF_3CHO data were reanalysed using a Hamiltonian, based on that given by Lewis et al. [3],

$$\hat{H} = -\frac{d}{d\alpha}[F_0 + F_3 \cos(3\alpha)]\frac{d}{d\alpha} - D_F^{(1)}\frac{d^4}{d\alpha^4} + \frac{1}{2}\sum_n V_{3n}[1 - \cos(3n\alpha)], \qquad (1)$$

although not all possible parameters were included at any one time. Energy levels were calculated using sine and cosine basis functions, the torsional energy matrix being diagonalised numerically. CF_3NO data were adjusted by means of weighted non-linear least-squares fitting, weighting being essential because of the greater precision of the microwave Δ_0 value [4] compared with the uncertainties in the torsional spacings from the optical data. For CF_3CHO, less

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data are available and numerical solutions were obtained by fitting to a data set which contained redundant information.

3. Trifluoronitrosomethane

The microwave spectrum of CF_3NO has been analysed by Turner and Cox [4] using the internal axis method. Their analysis gave the ground-state torsional splitting: $-\Delta_0 = \nu(0E-0A) = 8.59(2)$ MHz, which, with $F = 2.25$ cm^{-1} calculated from the structure, gave $V_3 = 269$ cm^{-1} for a single-parameter potential. This model predicts a torsional frequency $\bar{\nu}(1E-0E) \approx 67$ cm^{-1}.

Following the microwave work, DeKoven et al. [1] observed torsional sidebands in the A–X electronic spectrum. They reported accurate torsional spacings up to $v = 5$ for the electronic ground state, giving $\bar{\nu}(1E-0E) = 58(1)$ cm^{-1}. Then, estimating $F = 2.23$ cm^{-1} from the microwave structure [4], reported that their data could not be reproduced using the microwave V_3 value. They therefore chose to ignore the microwave torsional data on the basis that levels closer to the top of the barrier were a more reliable indicator of barrier height. Consequently they used a value of $V_3 = 202(10)$ cm^{-1} with $F = 2.23(1)$ cm^{-1}. This model, however, predicts $-\Delta_0 = 46.5$ MHz (cf. 8.59 MHz observed), which gives a completely wrong scaling factor for the microwave splittings, a difficulty which apparently went unnoticed. Moreover, the model does not fit their own data within experimental error, and a much better fit was obtained if both V_3 and F were taken as fitting parameters, but no significance was attached to this at the time.

Here we fit the combined microwave and optical torsional data simultaneously. It was expected that the parameters of the Hamiltonian (1) would be sufficient, but it was found that the data could not be fitted with any parameter combination unless F_0 was allowed to depart from the structural estimate. Once this was done however, three parameters, either F_0, V_3 and V_6 or F_0, F_3 and V_3, were sufficient to fit all the data. Furthermore, both sets of parameters were good enough to confirm accurately tentative assignments which had been given [1] up to $v = 8$. These additional torsional spacings were therefore estimated from the published spectra [1] and added, with generous uncertainties, to the data set.

The fit to F_0, V_3 and V_6 is given in table 1. A variety of suitable parameter sets is also given in table 2. Note that F_0 and V_3 are well determined, and that the inclusion of V_9 and V_{12} terms is not justified by the data. F_3 and V_6 cannot be simul-

Table 1
Torsional data for CF_3NO

$v'\sigma'-v\sigma$	Obs. (cm^{-1})	Obs. − calc. (cm^{-1})	Weight (cm^2)
0E–0A	0.00028646(67)	0.00000000	2.228×10^{12}
1E–0E	58(1)	−0.38	1.0
2E–0E	112(1)	−0.50	1.0
3E–0E	161(1)	1.21	1.0
4E–0E	202(2)	−1.40	0.25
5E–0E	228(3)	−2.28	0.111
5A–0A	257(5)	−0.48	0.04
6A–0A	261(5)	0.43	0.04
6E–0E	295(10)	0.98	0.01
7E–0E	337(10)	3.20	0.01
7A–0A	378(10)	−0.04	0.005
8A–0A		−0.07	0.005

$F_0 = 1.9822(42)$ cm^{-1}, $V_3 = 238.4(1.6)$ cm^{-1}, $V_6 = -5.8(1.6)$ cm^{-1}

weighted standard deviation of fit = 0.58 cm^{-1}
60 basis functions

Table 2
Parameters (cm^{-1}) from various least-squares fits (cm^{-1}) of torsional data for CF_3NO

F_0	F_3	$D_F^{(1)}$	V_3	V_6	V_9	V_{12}	σ_{fit}
1.9822(42)	–	–	238.4(1.5)	−5.8(1.6)	–	–	0.582
1.9894(66)	−0.194(55)	–	239.3(1.9)	–	–	–	0.588
1.9822(45)	–	0.0000(2)	238.3(2.9)	−5.8(1.8)	–	–	0.617
1.9768(41)	–	–	237.0(1.4)	−2.5(1.9)	−4.6(1.9)	–	0.470
1.9761(38)	–	–	236.1(1.5)	−1.0(2.1)	−7.2(2.7)	3.6(2.8)	0.451
1.9892(81)	−0.193(62)	0.0000(3)	239.2(3.3)	–	–	–	0.624
1.9861(44)	0.150(56)	–	237.2(1.9)	−10.0(fixed)	–	–	0.566
1.9909(52)	0.222(55)	–	236.6(1.9)	−12.0(fixed)	–	–	0.555

taneously varied because, to first order, there is a linear relationship between F_n and V_{n+3} [5]. $D_F^{(1)}$, the coefficient of P_α^4, was determined to be negligible, as expected from, for example, CHF_3, where $D_K = 2.7 \times 10^{-7}$ cm^{-1} [6].

The above results prompted a reconsideration of the structure. Published electron diffraction data [7] and microwave data [4] were used. The procedure for calculating the internal rotation constant, F, from various trial structures, was as follows: the moment of inertia of the CF_3 top, I_α, and the principal moments, I_a, I_b, I_c, were determined from the geometry of the trial structure rather than from the measured rotational constants. Structures were all defined with a symmetric CF_3 group rotating about an axis (z) which was not coincident with the C–N bond, i.e. the CF_3 group was tilted slightly away from the oxygen atom. F was then computed from the conventional formula

$$\frac{h}{8\pi^2 F} = I_{eff} = I_\alpha \left(1 - \sum_{g=a,b,c} \lambda_{gz}^2 \frac{I_\alpha}{I_g}\right) \tag{2}$$

(λ_{gz} are direction cosines), which, since CF_3NO has an *ab* plane of symmetry, reduces to

$$I_{eff} = I_\alpha [1 - (I_\alpha/I_a) \cos^2\theta_{az} - (I_\alpha/I_b) \sin^2\theta_{az}] \tag{3}$$

(θ_{az} is the angle between the a principal axis and the z axis). Using the above method, the electron diffraction structure [7] gave $F = 2.184$ cm^{-1}. The microwave structure [4] gave $F = 2.165$ cm^{-1}. A structure obtained by using the C–F bond length from electron diffraction [7] and fitting to the isotopic rotational constants [4] gave $F = 2.137$ cm^{-1}. The latter structure is the one referred to in later discussions. The good agreement between the three structures indicated that there is almost certainly a systematic difference between the structural F and F_0 (1.982 cm^{-1}).

This discrepancy cannot be explained on the basis of torsion–other vibrational coupling in the usual sense of mixed wavefunctions, because molecules with light internal rotors do not show the discrepancy despite their much higher torsional frequency. Furthermore, Quade [8,9] has shown, to a zeroth-order approximation, that the torsion–other vibration interaction can be absorbed into the effective potential of a single-degree-of-freedom model without affecting the internal rotation constant. Another possibility is that the discrepancy can be attributed to centrifugal distortion effects. The present results, however, indicate that the P_α^4 contribution to F is very small. Furthermore, molecules with light internal rotors would again be expected to exhibit the discrepancy if centrifugal distortion were the cause.

Eq. (3), if it is interpreted in the usual way, is evidently an inaccurate estimator of F_0 and is inaccurate in a way which worsens for heavy internal tops. Also, if a single quantity is responsible for the error, then that quantity must lie in the bracketed part of the equation, because, for light internal rotors, $I_{eff} \approx I_\alpha$: the term in brackets approaches 1 and I_{eff} becomes insensitive to all errors except those in I_α. For CF_3NO uncertainty in θ_{az} will be the greatest contributor to uncertainty in F. This comes about because $(I_\alpha/I_A) \cos^2\theta_{az} \to 1$ and the moments of inertia are well determined from the microwave data, all being much too large to be significantly affected by inertial defect considerations.

Eq. (3) may be rearranged as follows:

$$\cos\theta_{az} = \frac{(1 - I_{eff}/I_\alpha - I_\alpha/I_b)^{1/2}}{(I_\alpha/I_a - I_\alpha/I_b)^{1/2}} . \tag{4}$$

If we take I_α, I_a and I_b as known constants it is thus possible to calculate the value of θ_{az} (θ'_{az} say) which corresponds to F_0. Our least-squares structure gave (in u Å^2) $I_\alpha = 89.13, I_a = 90.59$ and $I_b = 157.83$. These give $\theta'_{az} = 25.78°$. From the structure, $\theta_{az} = 24.56°$. Thus a small change of ≈1.2° in θ_{az} will bring F into coincidence with F_0. Furthermore, the required shift corresponds to a rotation of the z axis towards the C–N bond, where $\theta_{a,\mathrm{C-N}} = 28.31°$.

The internal rotation constant F in a particular torsional state should be equated to $F_0 + F_3\langle\cos(3\alpha)\rangle$. F_0 will correspond more closely to the structural F for higher torsional states. In the ground state $\langle\cos(3\alpha)\rangle$ is ≈0.85, so if we fix V_6 at the reasonable value of -11 cm^{-1} a value for F_3 of 0.186 cm^{-1} is obtained from the fit to the torsional data (see table 2) and F agrees with the structural value. The difference $F - F_0$ arising from torsional averaging, is evidently large for heavy tops and is presumably due to the sensitivity of F to θ_{az} as indicated in the previous paragraph. The value of θ_{az} itself is sensitive to the tilt angle ($\theta_{a,\mathrm{C-N}} - \theta_{az}$) of the top and hence to the torsional averaging process. Rotation of the CF_3 group results in three identical potential minima, yet the group cannot be symmetric because it does not exist in a symmetric environment. The measured tilt therefore hides the complexity of the paths taken by the fluorine atoms when the CF_3 group rotates relative to the molecular frame. It is in effect a means of reconciling the structural data, which demands that the CF_3 group be asymmetric about the C–N bond, with the requirement of the tunnelling model, which demands that the group be symmetric about its internal rotation axis. Resolution of this paradox requires that the bond axis and the internal rotation axis are allowed to be different. (It should be noted that if F_3 has a negative value as would be implied by solutions for which $V_6 = 0$ to -5.8 cm^{-1} then the difference between the spectroscopic value $F_0 + F_3\langle\cos(3\alpha)\rangle$ and the structural F would remain and a further, more complicated explanation, would be required.)

The idea that the molecule possesses a symmetric group constrained to rotate about the z axis is only one extreme view of the internal rotation process. The other extreme is that the molecule possesses an asymmetric group constrained to rotate about the C–N bond. The real situation is a superposition of the two, where the former case applies in the free-rotation limit and the latter case applies in the limit of infinitesimal torsional amplitude. The internal rotation constant for CF_3NO executing an infinitesimal rotation about the C–N bond was estimated to be 1.910 cm^{-1} by applying Pitzer's equation [10] to the structure. The result for symmetric rotation about the z axis has already been given as 2.137 cm^{-1}. $F_0 = 1.982$ cm^{-1} clearly lies between the two.

4. Trifluoroacetaldehyde (Fluoral)

The microwave spectra of CF_3CHO and CF_3CDO have been studied in detail by Woods [11,12], who analysed spectra for both species in their $v = 0$ and $v = 1$ torsional states. For CF_3CHO Woods reported $V_3 = 309(26)$ cm^{-1}, with $F = 2.09$ cm^{-1} from structure, which gives a torsional frequency of ≈76 cm^{-1}. Berney [2] recorded the gas-phase infrared spectrum of CF_3CHO and observed the torsional band at 55 cm^{-1}. The same discrepancy was found for CF_3CDO. In that case the torsional band was obtained at ≈52 cm^{-1} whereas Woods' data predict ≈71 cm^{-1}.

Partially determined structures for CF_3CHO have been given by Schwendeman [13] and Woods [12]. We refined these by obtaining the C–H bond length from the stretching frequency [14] and then fitting to the available rotational constants extrapolated to $v = -\frac{1}{2}$ in the torsion. This structure gave $\theta_{az} = 20.97°$ and $\theta_{a,\mathrm{C-C}} = 22.99°$, a tilt of 2.01°. Evaluating F about the z axis using eq. (3) gave 2.107 cm^{-1}. Evaluating F about the C–C bond using Pitzer's equation [10] gave 1.991 cm^{-1}.

For CF_3CHO Woods reported $\nu(0E-0A) = 1.53$ MHz and $\nu(1A-1E) = 75$ MHz. Berney gave $\bar{\nu}(1-0) = 55$ cm^{-1}. We first attempted to fit these data with F_0 fixed at 2.1(1) cm^{-1} but were unable to do so with "reasonable" parameters in the Hamiltonian (1). When F_0 was allowed to vary we obtained 1.66 cm^{-1}, which is obviously much too low and casts doubt on the infrared measurement.

Part of the far-infrared spectrum of CF_3CHO is reproduced in Berney's paper [2]. The torsional band is a broad feature covering ≈30 cm^{-1}. Berney chose to identify a small dip in the middle of the band at 55 cm^{-1} as the torsional fundamental. However, our calculated spectra indicate that this absorption is in fact the torsional hot-band profile and the fundamental is predicted to lie in the upper edge of the observed band (≈66 cm^{-1}). Berney did make observations at two temperatures in an attempt to resolve the question of hot-bands, but our Boltzmann calculations indicate that not much difference would have been seen under the experimental conditions used. A re-examination of the torsional band is clearly desirable but taking a value for $\bar{\nu}(1-0) = 66(5)\ \mathrm{cm}^{-1}$, in conjunction with the microwave data, gives a sensible result (in cm^{-1}): $F_0 = 1.97(14)$, $V_3 = 305(25)$ and $V_6 = -8.7(1.2)$. The V_6 value obtained agrees well with the contribution to the effective V_6 from the torsion–other vibration interaction calculated by Quade [9] to be $-6.51\ \mathrm{cm}^{-1}$. The difference between F and F_0 is about half the value found for CF_3NO but then the CF_3 tilt is also found to be smaller in CF_3CHO.

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